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COMPUTATIONS OF VIBRATIONAL INFRARED  
FREQUENCIES OF SELECTED AMINES

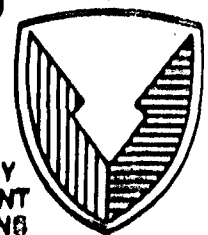
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# COMPUTATIONS OF VIBRATIONAL INFRARED FREQUENCIES OF SELECTED AMINES

## 1. Introduction

The work that is described in the present report constitutes a continuation of our computation of vibrational infrared frequencies of organic molecules. In a previous technical report<sup>1</sup> we presented computations on alcohols, mercaptans and sulfides. In the present report we describe computations on a group of amines. We investigated (1) two primary amines, methyl amine and ethyl amine and the corresponding chloro-substituted molecules, (2) two secondary amines, dimethyl amine and diethyl amine and the corresponding chloro-substituted molecules dichloromethyl amine and methyl, chloromethyl amine and (3) three tertiary amines, trimethyl amine, triethyl amine and methyl, diethyl amine.

The theoretical prediction of vibrational infrared spectra is of practical importance for the identification of known and unknown compounds. Of course, if a compound has been synthesized and if its infrared or Raman spectrum have been measured then the compound is readily identified by comparing its spectrum with the available experimental spectrum. However, in many instances we would like to identify an unknown compound by measuring its vibrational infrared or Raman spectrum or we would like to identify a molecule of known composition that has not yet been synthesized or cannot easily be synthesized. In the latter case it would be helpful if the vibrational frequencies and intensities could be predicted theoretically since they cannot be determined experimentally. It should be noted also that the computation of a vibrational infrared spectrum of an organic molecule is considerably cheaper than the synthesis of the molecule and the experimental determination of its spectrum.

We will show that vibrational frequencies may be computed by means of ab-initio quantumchemical methods with possible errors that vary between 1 and 12%, depending on the type of vibrational mode. However, it is well known that in organic molecules many of the vibrational modes are localized and that many functional groups have characteristic frequencies that do not vary much between different molecules. We feel therefore that the accuracy of computed frequencies may be improved by considering groups of similar molecules and by introducing correction factors that bring the computed frequencies in line with the available experimental data. We have found that it is not advisable to use a uniform correction factor for all vibrational modes. It is preferable instead to introduce different correction factors for different types of vibrational modes, for instance we should differentiate between C-H, C-C and C-Cl stretch frequencies, H-C-H bend frequencies, etc. In this way the unknown vibrational frequencies are predicted by computations and by interpolation or extrapolation of the available experimental data. By following this procedure the accuracy of frequency predictions may be improved significantly.

## 2. Computational Methods

Our computations are based on the Gaussian 82 or 86 Program Package<sup>2</sup>. The computation of vibrational frequencies by this method is extensively discussed in the book by Hehre, Radom, von Schleyer and Pople<sup>3</sup>. The accuracy of the results depends on the type of basis set that is used and on the type of computation, Hartree-Fock, Hartree-Fock with configuration interaction, etc. We performed some preliminary computations and we concluded that the use of the straightforward Hartree-Fock procedure (no CI) with the 3-21G basis set constitutes a satisfactory compromise of enough accuracy and reasonable computational effort. Our preliminary work suggests also that the results obtained from the STO-3G basis set are not of sufficient accuracy to be of practical use. The use of more elaborate basis sets than 3-21G and the addition of configuration interaction does not improve the accuracy of the frequency calculations significantly but it requires considerably more computational efforts. All our observations are consistent with the analysis and discussion presented by Hehre et al<sup>3</sup>. We decided therefore to use the HF/3-21G option for all our frequency calculations. It should also be noted that we are interested in large organic molecules and that in many of our computations the use of basis sets larger than 3-21G is not feasible. Since we wish all our theoretical results to be consistent we feel that the use of the HF/3-21G option constitutes a suitable compromise of accuracy and manageable computational effort.

In the Gaussian 86 Program Package the vibrational modes and frequencies are all derived by assuming the harmonic approximation. First the molecular geometry is optimized so that all gradients of the molecular energy with respect to nuclear displacements are zero. Next, the molecular energy is computed in a number of points near each optimized geometry point. Here there are two different options. In the analytical option the second derivatives of the molecular energy relative to the nuclear displacement coordinates are evaluated analytically. In the numerical option the molecular energy is actually computed at six points around each equilibrium position. In both cases the vibrational modes and frequencies are then computed by assuming a harmonic potential. This assumption is convenient but it is not always correct and it may be responsible for some differences between theory and experiment.

We have considered a total of eleven amines and corresponding chloro-substituted amines and we discuss the primary, secondary and tertiary amines separately in the following three sections.

## 3. Results

### 3.1 Primary amines

We have computed the 3-21G optimized geometries and the corresponding vibrational frequencies of four primary amines: methyl amine, chloromethyl amine, ethyl amine and 2-chloromethyl amine. The computed frequencies are all listed in Table I.

The primary amines have a  $\text{NH}_2$  group and this functional group has five characteristic frequencies: two N-H stretch frequencies around  $3700\text{ cm}^{-1}$ , two H-N-H bend modes around  $1250\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  and a  $\text{NH}_2$  wagging motion around  $750\text{ cm}^{-1}$ . In addition there is a N-C stretch mode with a frequency which varies between  $1100$  and  $1250\text{ cm}^{-1}$ . This group of six frequencies is characteristic of all primary amines.

The presence of the chlorine atom may be detected by observing the C-Cl stretch frequency, which is at  $505\text{ cm}^{-1}$  for the methyl compound and at  $626\text{ cm}^{-1}$  for the ethyl compound. There is no experimental information available for the chloro-substituted molecules and we cannot offer any explanation for the difference in C-Cl stretch frequency between the two molecules.

All molecules exhibit a number of C-H stretch modes, the number is of course equal to the number of C-H bonds in the molecule. In ethyl amine we identify two stretch modes that we denote by  $\text{C}_m\text{-H}$  modes and which are localized in the middle  $\text{CH}_2$  group. The others, which we denote by  $\text{C}_e\text{-H}$  modes are localized in the  $\text{CH}_3$  or  $\text{CH}_2\text{Cl}$  end groups. All C-H stretch frequencies are grouped together in a narrow range between  $3130$  and  $3440\text{ cm}^{-1}$ . The ethyl amines also exhibit a C-C stretch mode around  $950\text{ cm}^{-1}$ .

It is not easy to identify and characterize the various H-C-H bending modes because most of them are delocalized and we often have difficulty even assigning them to a specific  $\text{CH}_2$  or  $\text{CH}_3$  group. An exception is the  $\text{CH}_2$  or  $\text{CH}_3$  wagging mode, which occurs at  $900$  or at  $1100\text{ cm}^{-1}$ , we have listed those separately. All other H-C-H bending modes are listed as a group.

We were unable to find experimental information for the two chloro-substituted compounds but there is an abundance of experimental information available for methyl amine and there is a report of the Raman spectrum of ethyl amine. We present a comparison of our computed frequencies and the experimental data in Table II.

In the case of methyl amine we compare our computed values with the infrared frequencies reported by Owen and Barker<sup>4</sup> and with the Raman frequencies reported by Kohlrausch<sup>5</sup> and by Kirby-Smith and Bonner<sup>6</sup>. We found an additional four or five reports on the IR and Raman spectra of methyl amine but the experimental results seem to be quite consistent and we did not see any point in listing them all. Kohlrausch<sup>5</sup> also reported the Raman spectrum of ethyl amine. We were not able to find any other experimental information for that molecule.

It may be seen in Table II that there is a systematic difference between the computed and the experimental C-H and N-H stretch frequencies, the ratio between the experimental and the computed values is  $0.9$  with a possible deviation of  $0.015$ . In the group of H-C-H bend frequencies the corresponding ratio is slightly smaller; it is  $0.875$  with a possible deviation of  $0.01$ . In the case of the other frequencies, the N-C and C-C stretch, the H-N-H bend and the  $\text{CH}_2$  and  $\text{NH}_2$  wag the computed and the experimental frequencies are fairly close together and it is not practical to introduce any correction factor other than unity.

### 3.2 Secondary amines

We have computed the 3-21G optimized geometries and the corresponding vibrational modes and frequencies of four secondary amines: dimethyl amine, diethyl amine, dichloromethyl amine and methyl, chloromethyl amine.

The secondary amines have a NH group and this functional group has three characteristic vibrational modes, a N-H stretch mode with a frequency between 3700 and 3800  $\text{cm}^{-1}$  and two N-H bend modes, the first has a frequency around 700  $\text{cm}^{-1}$  and the second has a frequency around 1650  $\text{cm}^{-1}$ . The secondary amines are also characterized by a C-N-C scissor mode with a frequency between 400 and 500  $\text{cm}^{-1}$  and two C-N stretch modes with frequencies between 1000 and 1300  $\text{cm}^{-1}$ . These six characteristic frequencies are typical of the secondary amines. Note that the C-N stretch frequencies of dimethyl and diethyl amine are practically identical, they are at 1194 and at 1242  $\text{cm}^{-1}$ . The lower frequency is shifted downwards by as much as 200  $\text{cm}^{-1}$  by chlorine substitution and the higher frequency is shifted upwards by about 50  $\text{cm}^{-1}$ .

All four molecules have one N-H stretch mode and as many C-H stretch modes as there are C-H bonds. The C-H stretch frequencies are grouped in a fairly narrow range between 3100 and 3450  $\text{cm}^{-1}$ . The chloro-substituted molecules have one or two C-Cl stretch modes with frequencies between 500 and 600  $\text{cm}^{-1}$ . Diethyl amine exhibits two C-C stretch modes around 1000  $\text{cm}^{-1}$  and two N-C-C bend modes around 1200  $\text{cm}^{-1}$ . In addition we have identified two  $\text{CH}_2$  wagging modes in the dimethyl compounds and an additional  $\text{CH}_2$  wag in the diethyl compound.

We had difficulty identifying the many H-C-H bending modes since they correspond to delocalized vibrational modes involving the whole molecule. Therefore we have just listed the corresponding frequencies as a group in numerical order.

The Raman spectrum of dimethyl amine was reported by Kohlrausch<sup>5</sup> and the IR spectrum of diethyl amine is listed in the Aldrich Library of Infrared Spectra<sup>7</sup>. We were not able to find experimental information on the chloro-substituted amines.

We have listed the experimental and our computed frequencies of dimethyl and diethyl amine in Table IV. The ratio between the experimental and the computed C-H and N-H stretch frequencies is the same as for the primary amines, the same is true for the H-C-H bend frequencies. The assignment of the other frequencies (1045, 1099 and 1134  $\text{cm}^{-1}$ ) of diethyl amine is less straightforward. We have assigned 1045 to the computed 1071 wag frequency, 1099 to the 1192 C-N stretch frequency and 1134 to the 1241 C-N stretch frequency, but these assignments are subject to some uncertainties since our computations do not predict intensities.

### 3.3 Tertiary amines

We have computed the 3-21G optimized geometries and the corresponding vibrational modes and frequencies of three tertiary amines: trimethyl amine, triethyl amine and methyl, diethyl amine. The first molecule was computed on a Microvax and the latter two molecules were computed at the Cray computer at the Alabama Supercomputer Network. We list all computed frequencies in Table V.

The tertiary amines are characterized by three C-N stretch mode frequencies and by three C-N-C bend mode frequencies. If there is  $c_{3v}$  symmetry two of the stretch modes and two of the bend modes are doubly degenerate, in other words, two of the stretch frequencies are equal and two of the bend frequencies are equal. We found that trimethyl amine and triethyl amine are extremely close to  $c_{3v}$  symmetry, the nitrogen and carbon skeletons have  $c_{3v}$  symmetry but the rotation of the C-H bonds cause a slight distortion of the symmetry. It may be seen in Table V that for both molecules two of the C-N stretch frequencies and also two of the C-N-C bend frequencies are very close together, this is consistent with a very slightly distorted  $c_{3v}$  structure. In methyl, diethyl amine there is no  $c_{3v}$  symmetry and the C-N frequencies are all different.

In addition to the C-N modes each molecule has a number of C-H stretch modes equal to the number of C-H bonds in the molecule and a number of C-C stretch modes equal to the number of C-C bonds. All these stretch modes and the six C-N modes are clearly identified. There are also three  $CH_3$  wag modes in each molecule and as many  $CH_2$  wag modes as there are  $CH_2$  groups. The other H-C-H bend modes are delocalized throughout the molecules and we list them as a group in numerical order.

The Raman spectrum of trimethyl amine has been reported by Kohlrausch<sup>5</sup> and the IR spectrum of triethyl amine has been reported in the Aldrich Library<sup>7</sup>. We present a comparison of the computed and the experimental frequencies in Table VI. Since there are no N-H bonds we do not observe any N-H stretch or bend frequencies. Some of the C-H stretch frequencies are very close together and we suspect that many of the experimental IR lines represent two or more of the computed frequencies. The ratio between the experimental and the computed C-H stretch frequencies is again 0.90 with a possible deviation of 0.01. We have also identified two C-N stretch frequencies and two C-N-C bend frequencies, in each case one mode is doubly degenerate. The ratio between the experimental and the computed values is 0.95 for the C-N stretch frequencies and 0.89 for the C-N-C bend frequencies. In the triethyl molecule we have also identified the  $CH_2$  and the  $CH_3$  wag modes and a C-C stretch mode. The other frequencies correspond to H-C-H bend modes, here the ratio is again equal to 0.875.

#### 4. Conclusions

We feel that our computations of the vibrational modes and frequencies of the eleven amines constitute a useful basis for the theoretical prediction of the vibrational frequencies of amines. We mentioned already that triethyl amine and methyl, diethyl amine were computed on a Cray Supercomputer, we should add that all the other molecules were computed on a Microvax. We believe that computations on larger tertiary amines or on chloro-substituted tertiary amines may be successfully completed on a Cray Supercomputer, but we do not believe that molecules of such size can be handled by a Microvax.

It may be seen in Tables II, IV and VI that the differences between computed and experimental frequencies are at most 12%. After introducing correction factors the errors may be reduced to 1 or 2%. Here it is important to note that different correction factors should be used for different types of vibrations. It is not advisable to use the same correction factor for all types of vibrational modes since this leads to significantly larger errors in the theoretical predictions.

It should also be noted that certain types of vibrational modes are much more readily identified than others. For instance, the C-N stretch modes and the C-N-C bend modes are clearly recognized in all amines. On the other hand, many of the H-C-H bend modes are delocalized throughout the whole molecule and we find it difficult to label these modes or to differentiate between them. Fortunately, the H-C-H bend frequencies are not all that relevant for identification purposes, since they suggest only the presence of C-H bonds and usually we know that already. The more relevant characteristic frequencies such as the C-N stretch and bend modes, the N-H bend and stretch modes, the C-Cl stretch mode, etc, are clearly identified and assigned.

In summary, we believe that the computations of the vibrational frequencies of a group of similar amines may lead to accurate frequency predictions if the computations are combined with an analysis of the available experimental information.

Table 1. Computed frequencies of methyl amine, ethyl amine, chloromethyl amine, and 2-chloroethyle amine.

	methyl am.	ethyl am.	chlorom. am.	chloroeth. am.
torsion	316.7	434.8	483.9	479.0
C-Cl stretch	-	-	504.8	625.9
NH <sub>2</sub> wag	753.2	764.8	717.8	776.9
C-C stretch	-	933.0	-	960.7
N-C stretch	1095.9	1152.3	1250.7	1170.3
CH <sub>2</sub> wag	1047.2	900.7	927.9	922.6
	-	1079.1	-	1103.7
CH <sub>3</sub> bend	1456.1	1386.6	1396.6	1301.9
	1614.7	1457.1	1488.8	1424.0
	1680.5	1547.1	1649.7	1468.3
	1702.1	1567.5	-	1555.3
	-	1663.6	-	1615.1
	-	1673.9	-	1671.7
	-	1694.3	-	-
H-N-H bend	1256.0	1242.3	1221.1	1263.7
	1851.0	1694.3	1649.7	1671.7
C <sub>m</sub> stretch	-	3131.1	-	3176.3
	-	3254.6	-	3224.7
C <sub>e</sub> stretch	3134.8	3231.2	3348.5	3318.3
	3229.8	3254.6	3441.6	3403.6
	3264.5	3282.6	-	-
N-H stretch	3678.0	3665.0	3752.4	3686.6
	3774.6	3762.1	3860.7	3786.8

Table 2. Comparison of computed and experimental frequencies of methyl amine and ethyl amine.

methyl amine				ethyl amine	
comp	IR <sup>4</sup>	Ram <sup>5</sup>	Ram <sup>6</sup>	comp	Ram <sup>5</sup>
753	780	-	781	435	414
1096	-	1039	1044	933	889
1256	-	-	-	1079	1046
1456	-	-	-	1152	1082
1614	1385	-	-	1242	1122
1680	1470	1466	1460	1386	1223
1702	-	-	-	1457	1293
1851	1625	-	-	1547	1376
3135	2820	2808	2820	1664	1450
3230	2930	2879	2883	3131	2834
3264	2964	2945	2960	3196	2867
3678	3360	3312	3360	3231	2904
3775	3410	3372	3470	3254	2926
-	-	-	-	3282	2960
-	-	-	-	3664	3305
-	-	-	-	3762	3367

Table 3. Computed frequencies of dimethyl amine, diethyl amine, dichloromethyl amine and methyl, and chloromethyl amine.

	dimeth.am.	dieth.am.	dichlorom.am.	meth,chlorom.am.
C-N-C bend	399.6	506.9	489.2	441.9
C-Cl stretch	-	-	565.1	521.7
	-	-	599.7	-
N-H bend	717.7	689.4	753.8	681.0
	1634.8	1639.3	1700.0	1647.1
C-N stretch	1195.5	1192.5	1013.3	971.1
	1243.3	1241.4	1256.1	1290.3
C-C stretch	-	986.5	-	-
	-	1071.3	-	-
CH <sub>2</sub> wag	-	864.6	-	-
	-	905.7	-	-
CH <sub>3</sub> wag	969.5	925.2	975.3	1059.9
	1130.1	1275.8	1153.7	1210.1
N-C-C bend	-	1170.5	-	-
	-	1326.5	-	-
C-H bend	1290.5	1436.1	1328.9	1262.1
	1375.0	1454.6	1420.6	1388.8
	1599.9	1526.4	1446.2	1435.9
	1627.3	1533.2	1460.5	1613.9
	1667.4	1566.8	1630.6	1663.4
	1678.7	1569.4	1656.0	1679.1
	1694.6	1639.3	-	1698.9
	1701.6	1664.3	-	-
	-	1667.0	-	-
	-	1671.4	-	-
	-	1675.6	-	-
	-	1680.9	-	-
	-	1702.1	-	-
C-H stretch	3116.8	3155.8	3226.6	3200.2
	3122.7	3161.7	3329.5	3260.7
	3220.2	3193.8	3413.5	3291.9
	3223.8	3201.3	3416.3	3344.1
	3259.9	3202.0	-	3440.4
	3261.9	3205.9	-	-
	-	3259.0	-	-
	-	3261.6	-	-
	-	3272.3	-	-
	-	3272.6	-	-
N-H stretch	3713.3	3700.4	3789.8	3783.4

Table 4. Comparison of computed and experimental frequencies of dimethyl amine and diethyl amine.

dimethyl comp	amine Ram <sup>5</sup>	diethyl comp	amine IR <sup>7</sup>
400	390	-	-
717	826	689	724
970	931	1071	1045
1195	1078	1192	1099
1375	1236	1241	1134
1634	1438	1276	1186
1701	1472	1436	1264
-	-	1454	1282
-	-	1526	1325
-	-	1568	1370
-	-	1639	1449
3116	2776	3155	2800
3122	2816	3202	2880
3220	2890	3272	2956
3713	3343	3700	3268

Table 5. Computed frequencies of trimethyl amine, triethyl amine and methyl, and diethyl amine. Relative IR intensities are in parentheses.

vibration	trimeth. am.	trieth. am.	me.triet. am
C-N stretch	841.1	769.8 (11)	787.5 (13)
	1124.9	1149.9 (36)	1129.4 (33)
	1125.0	1150.0 (36)	1155.7 (40)
C-N bend	1330.8	1280.3 (11)	1294.1 (14)
	1412.8	1355.0 (23)	1351.7 (16)
	1412.9	1355.0 (23)	1380.0 (17)
C-C stretch	-	983.3 (0)	974.2 (1)
	-	983.3 (0)	1038.3 (2)
	-	1053.8 (0)	-
CH <sub>2</sub> wag	-	880.7 (5)	889.0 (3)
	-	880.7 (5)	893.0 (3)
	-	884.9 (2)	-
CH <sub>3</sub> wag	1167.3	1197.6 (5)	1194.1 (6)
	1235.7	1211.4 (8)	1216.8 (5)
	1235.7	1211.4 (8)	1232.5 (5)
C-H bend	-	1453.4 (3)	-
	-	1462.8 (17)	1459.7 (15)
	-	1462.8 (17)	14373.6 (5)
	-	1533.9 (15)	1536.8 (19)
	-	1533.9 (15)	-
	-	1552.8 (12)	1546.0 911)
	-	1568.9 (7)	1567.0 980
	-	1568.9 (7)	1570.4 (6)
	-	1573.1 (5)	-
	1602.6	1661.4 (4)	1620.2 (0)
	1602.6	1661.4 (4)	1633.4 (6)
	1643.2	1662.6 (2)	1664.8 (3)
	1667.6	1668.1 (0)	1667.0 (3)
	1667.7	1675.8 (0)	1676.2 (1)
	1672.7	1675.8 (0)	1683.3 (5)
C-H stretch	1689.2	1684.0 (5)	1690.4 (4)
	1690.8	1684.1 (5)	1692.5 (15)
	1690.8	1689.9 (9)	-
	3144.4	3166.6 (7)	3157.3 (22)
	3144.5	3166.6 (7)	3159.4 (17)
	3157.4	3175.7 (157)	3168.9 (140)
	3196.7	3203.0 (0)	3200.7 (19)
	3196.9	3204.4 (13)	3203.8 (1)

Table 5. Computed frequencies of trimethyl amine, triethyl amine and methyl, and diethyl amine. Relative IR intensities are in parentheses. (Continued)

3199.6	3204.4 (13)	3205.9 (12)
3249.7	3213.9 (41)	3212.1 (50)
3254.1	3213.9 (41)	3216.9 (46)
3254.3	3215.3 (9)	3256.3 (41)
-	3263.2 (9)	3266.1 (31)
-	3264.6 (50)	3266.4 (39)
-	3264.6 (50)	3276.0 (52)
-	3271.3 (56)	3278.3 (43)
-	3274.1 (49)	-
-	3274.1 (49)	-

Table 6. Comparison of computed and experimental vibrational frequencies of trimethyl amine and triethyl amine.

trimethyl am.		triethyl am.	
comp	Ram <sup>5</sup>	comp	IR <sup>7</sup>
841	827	770	734
-	-	881	800
-	-	983	917
1124	1036	1150	1064
-	-	1198	1076
-	-	1211	1094
1330	1177	1280	1136
1413	1278	1355	1209
1668	1442	1676	1449
1690	1463	1690	1466
3144	2765	3176	2800
3196	2815	3214	2865
3250	2945	3264	2958
3254	2970	3274	2976

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